

Determination of Antimony trioxide from the back coated textile preparation

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Abstract

A simple and reproducible analytical method for determination of Antimony trioxide (ATO) is proposed, atomic absorption method was used. A simple quantitative extraction method is also proposed to extract ATO from textile backcoated sample. The proposed method is applied to determine the ATO in two different type of backcoated textile; type A contains ATO/ Hexabromocyclododecane (HBCD) and type B contains ATO/ Decabrodiphynl Ether (DBDE). A complete validation method for both extraction and analytical method is discussed. Linear calibration curve in range of 5 to 220 ng with detection limit of 5 ng

Keywords:

Antimony trioxide (ATO), Hexabromocyclododecane (HBCD), Decabromodiphenyl Ether (DBDE), Flame Retardant, backcoated textile, Textile

1. Introduction

Flame retardant materials are capable to prevent the spread of fires, or delay the time of flashover by slowing down the initial burning rate and thereby help to increase the time of flashover. Halogenated flame retardants are often the most effective flame retardant when both performance and cost are considered and they are widely used [1-5].

Antimony tri oxide (ATO) increases the flame retardant effect of halogenated flame-retardants, thereby minimising their addition level. Without ATO synergists, around twice as much halogen compounds would be needed to confer levels of flame retardancy required by legislation [6]. Thus the use of ATO in halogenated flame retardant applications not only reduces the costs but also could reduce the emission of halogenated flame retardant into the environment, moreover, incorporated ATO into the halogenated flame retardant often enables physical properties to be improved. In specialist applications it provides unique properties not easily obtained through other products e.g. friction modification, light stability of inorganic pigments, stable opacifiers for high temperature enamelling.

Antimony trioxide itself has no flame retardant function, however, when it is used together with halogenated compounds, the synergistic effect of the mixture creates the flame retardant properties. Antimony trioxide reacts with halogenated compound and creates the chemical compounds, which generate the flame retardant function through the

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following process: (i) stop action of thermal de-composite chain reaction under gas phase (Radical trap effect). (ii) Sealing action against oxygen under gas phase (Air sealing effect). (iii) The formation of carbonaceous char under the solid phase (Air sealing and adiabatic effect) [7].

Unfortunately, using antimony trioxide as flame retardants could cause many problems, since these material are physically combined with the material, they can easily leach and migrate out of textile and therefore absorbed by contact bodies in significant amounts, it was reported [8] that 0.8 mg of antimony will be absorbed daily just from the our mattresses. Moreover, antimony itself considered as the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure [9-11].

On the other hand antimony trioxide has a potential health effects; it may cause heart to beat irregularly or stop. Prolonged or repeated exposure may damage the liver and the heart muscle [12]. In fact, serious health effects were attributed to the direct contact with antimony trioxide including: (1) abortions in women exposed to airborne antimony in the workplace. (2) A reproductive effects; human exposure to antimony dust in the workplace has resulted in disturbances in menstruation [13]. (3) Adverse health effects in humans following antimony exposure appear to target on the respiratory and cardiovascular systems. Eye and skin irritation have also been noted. (4) Antimony may be found in the blood and urine several days after exposure [14,15]. (5) Finally a systemic study indicate that antimony trioxide is absorbed dermally in rabbits, systemic toxicity and death occurred in rabbits following dermal application of 8g kg⁻¹ antimony trioxide [16], and application of an unspecified dose of antimony trioxide in a paste of artificial acidic or alkaline sweat [17].

Recently, we published simple and reproducible analytical methods for determination of hexabromocyclododecane and Decabromodiphenyl ether from the back-coated textile [18,19]. Moreover, we studied the kinetics of the thermal and photolytic degradation of HBCD and its migration into biological fluid [20]. In this paper we continue our effects to study the issue of the flame retardant through the study of antimony trioxide. First we will propose an validated analytical method to analyze the antimony trioxide (ATO) from the back coated textile. Since ATO normally coexist with other halogenated flame retardant two different back-coated textile samples with different antimony trioxide concentration were analyzed; type (A) (ATO-HBCD) which contain antimony trioxide-Hexabromocyclododecane (Antimony trioxide is 3.6 %w/w of fabric) and type B (ATO-DPDE) contain antimony trioxide-Decabromodiphenyl ether (antimony trioxide is 4.3% w/w of fabric).

2. Experimental

2.1. Chemicals and reagents

Antimony trioxide (ATO), Sb₂O₃, where obtained from sigma-aldrich and used without further purification

2.2. Analytical method

The sampes were analyzed on Unicam 929 Atomic absorption system equipped with a hallow-cathode lamp of antimony wave length at 206 nm) and a cap type cuvette.

2.3. Validation and spiking of clay samples

Validation methods for the optimization of the analytical method were previously described [18,19]. Three sets of six samples of clay fabric samples free of ATO were

spiked with a known concentration of antimony trioxide dissolved in 1 M HCl and allowed to dry. The spiked samples were extracted using the same procedures used for the real samples and the recovery rate was calculated.

2.4. Sample treatment

2.4.1. Standard solutions

Antimony trioxide standard solutions were prepared by dissolving Antimony trioxide in 5 N Hydrochloric acid

2.4.2. Extraction method

ATO were extracted from the fabric samples (aged and unaged fabric samples) using a 5 N HCl solution, ATO were completely extracted under shaking condition for 6 hour and then 1 hour on ultrasonic bath. The extracted solutions were filtered and diluted when it is necessary.

3. Results and discussion

3.1. Validation of the analytical method

3.1.1. Calibration features

Linearity of the method was studied through the preparation and analysis of a set of calibration standard solutions containing antimony trioxide. Atomic absorption was used to determine the concentration of antimony trioxide in standard solutions to construct the calibration curve. Data are graphically presented in Fig 1. The calibration curve of this compound following a linear relationship with regression parameter is represented by equation (1):

$$y = 51.2 + (0.28) x \text{ with } R^2 \text{ equal to } 0.997. \quad (1)$$

Calibration results show that the calibration curve is linear and repeatable in the range of 5 to 220 ng with detection limit of 5 ng.

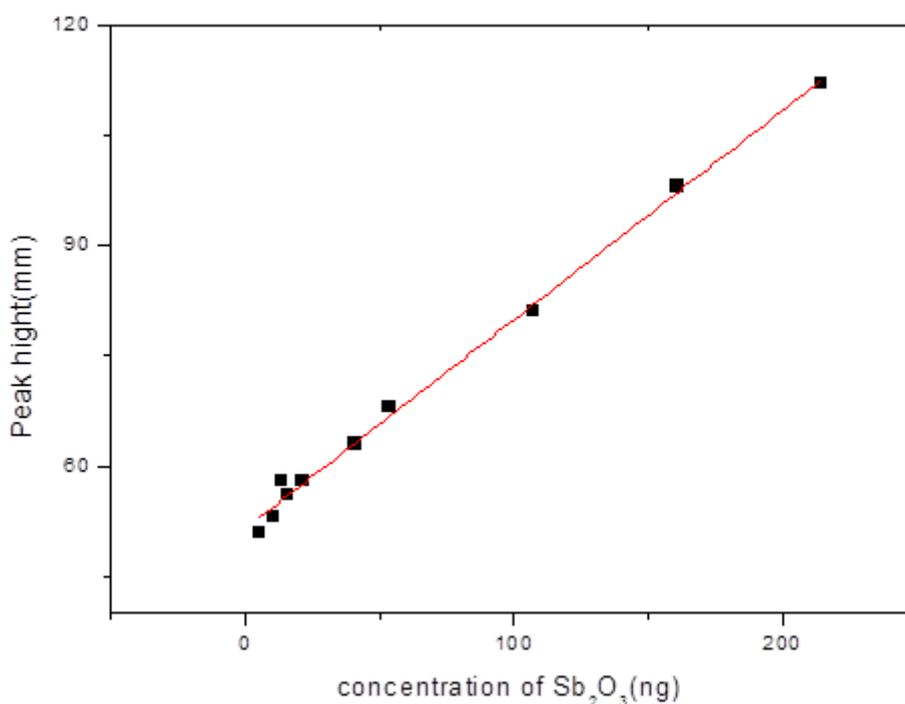


Fig.1 Calibration curve of ATO.

3.1.2 Validation of Extraction and Sampling Methods

The results of the three set of six sample of fabric free of Flame Retardant (FR) that were spiked with a known concentration of antimony trioxide are summarized in Table 1. The recovery percentages of 93.7 %, 90.9% and 91.2% for high, medium and low concentration levels, respectively, were achieved, which give an average recovery of $91.9 \pm 1\%$.

Table 1. Recovery of antimony trioxide from spiked Fabric.

Sample number	Sample weight lost (mg)	Nanogram of Sb ₂ O ₃ added	Nanogram of Sb ₂ O ₃ recovered	% Recovery
1	3.2	0.00	0.00	
2	6.4	1072	910.1±12	84.9
3	7.3	1072	1063.3 ±10	99.2
4	3.5	1072	936.7 ±15	87.4
5	8.3	1072	1116.5±4	104.2
6	7.2	1072	996.7±24	93.0
Mean recovery 1004 ng ± 86				94 ± 8
7	3.2		0.00	0.00
8	5.1	107.2	106.3±5	99.2
9	0.9	107.2	99.2 ±2	92.5
10	1.2	107.2	92.4 ±3	86.1
11	1.3	107.2	95.6 ±6	89.2
12	1.9	107.2	94.0 ±8	87.7
Mean recovery 98 ± 6				90.9 ± 5
13	3.2	0.00	0.00	
14	5.1	53.6	51.2±3	95.6
15	2.4	53.6	50.2±5	92.7
16	2.5	53.6	47.8±1	89.2
17	4.9	53.6	49.8 ±4	92.3
18	1.2	53.6	47.8±6	89.2
Mean recovery 49.4 ± 2				91 ± 3

3.1.3. Quantitative extraction of Textile sample

Two different backcoated textile samples with different antimony trioxide concentration were analyzed; type (A) (ATO-HBCD) which contain antimony trioxide-Hexabromocyclododecane (Antimony trioxide is 3.6 %w/w of fabric) and type (B) (ATO-DPDE) contain antimony trioxide-Decabromodiphenyl ether (antimony trioxide is 4.3% w/w of fabric), under identical extraction conditions. The weight lost during the extraction process on the fabric sample was also determined from recording the fabric weight before and after extraction. The results are summarized in Table 2. It was found that a $91 \pm 5\%$ of the theoretical concentration exists on the fabric contains ATO-HBCD flame retardant system, type A, compared $70 \pm 5\%$ recovered from fabric contains ATO-DBDPE flame retardants, type B, moreover both samples lose about 4% of their weight during the extraction procedure, the lost weight could be attributed to the recovered ATO. It is interesting to note the difference on the recovery of ATO from the two systems the low recovery of ATO from type B fabric (ATO-DPDPE system) is attributed to the attachment

of antimony trioxide with the polymer component of the fabric. In order to assess the absence of systematic errors, the proposed method was compared with another independent method [21-25] applied to the same set of textile samples. Again a relatively lower yield recovery is obtained for the ATO-DBDPE system which support the idea that the antimony trioxide is well attached to the textile contains DBDE. The regression method was applied. Considering the results obtained by the proposed method as y-values and those obtained by the independent method as x-values, the resulting straight line is $y = (0.3 \pm 0.4) + (0.94 \pm 0.05)x$. The corresponding Student's t tests on slope and intercept indicate, with a significance level of 5%, that there are not significant differences in the results obtained from either of the two methods, i.e, the proposed method is suitably validated. Despite the low recovery yield with respect to the label amount claimed by the manufacture, these results supports the possible applicability of the proposed method for routine and quality control analysis.

Table 2. Results of the extraction of Textile samples

Sample number	Sample weight(g)	Weight lost (mg)	Weight lost (%)	Theoretical Sb ₂ O ₃ (mg)	Recovery ¹ (%)
Clay sample					
1	0.3699	7.0	1.9	0.00	--
2	0.3693	5.2	1.4	0.00	--
Type A sample contain Antimony trioxide/HBCD					
3	0.3802	11.3	3.0	13.7	89.3± 2
4	0.3960	29.4	7.4	14.3	85.7 ± 0.3
5	0.3970	18.3	4.6	14.3	99.0 ± 1
6	0.3843	11.3	2.9	13.9	87.6 ± 0.8
7	0.3852	15.5	4.2	13.9	93.3 ±0.4
Average recovery (%)		91 ± 5			
Type B sample contain Antimony trioxide/DBPE					
8	1.5299	40.6	2.6	66.3	71.3 ± 0.3
9	1.4921	48.8	3.3	64.6	74.7 ± 0.5
10	0.3722	19.5	5.2	16.1	72.0 ±1.2
11	0.3736	18.3	4.8	16.2	63.9 ± 0.8
Average recovery (%)		70 ± 5			

¹Results are averaged of three repeated samples.

4. Conclusion

We proposed a sensitive, rapid, and practically simple method for determination of ATO from the back coated textile samples using atomic absorption. The proposed method does not require any sophisticated sample treatment, except the extraction. This method is validated with linear range between 5 to 220 ng and detection limit of 5 ng. Samples was applied to two types of real samples; ATO/HBCD and ATO/DBDPE, recovery of 91±5% of the theoretical concentration exists on the fabric contains ATO-HBCD flame retardant system, type A, was obtained compared to 70 ±5 % recovered from fabric contains ATO-DBDPE; the low recovery of ATO from type B fabric is attributed to the attachment of antimony trioxide with the polymer component of the fabric.

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